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Micro-Fabrication Method of Josephson Junctions without Etching Process

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Abstract

Intrinsic Josephson junctions (IJJs) were fabricated without etching process by introduction of an oxygen-depleted layer to the surface of the $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) single crystal changing the direction of current flow from in-plane (// *ab*) to out-of-plane (// *c*). This could be achieved by reducing the surface of the Bi-2212 single crystal. We took two methods to introduce the oxygen-depleted layer into the surface of Bi-2212 single crystal. One method is to introduce the oxygen-depleted layer by annealing the Bi-2212 single crystal in reductive atmosphere of H_2 gas. The Pt or Au electrodes for four-terminal measurement were deposited side by side on the surface of the Bi-2212 single crystal, and the Bi-2212 with electrodes was annealed in Ar+H_2 atmosphere. The resistivity-temperature (ρ-T) characteristics of the Bi-2212 single crystal changed from metallic ($d\rho/dT > 0$) to semiconducting ($d\rho/dT < 0$) behavior by annealing in Ar+H_2 atmosphere. In addition, hysteresis loop and voltage-jump, which are peculiar to IJJs, were observed in the current-voltage (I-V) characteristic of the sample annealed in Ar+H_2 atmosphere. It is known that Bi-2212 single crystals are reduced by H_2 annealing and the superconductivity of the reduced area is suppressed. Therefore, the surface of the Bi-2212 single crystal except for the masked area with the electrodes was reduced by Ar+H_2 annealing. As a result, the change in the direction of the current was caused due to the detour avoiding the reduced area, and IJJs were fabricated.
Another method to introduce the oxygen-depleted layer is to deposit metals with low Gibbs free energy and raising the temperature to exceed the activation energy for oxygen ions to move from Bi-2212 single crystal to the metal. We prepared the sample on which Al with low Gibbs free energy was deposited between the voltage terminals. Here, this sample is referred to as Al/Bi-2212 structures. The ρ-T characteristics of the as-prepared Al/Bi-2212 structure showed metallic behavior, whereas the ρ-T characteristics of the Al/Bi-2212 structure showed semiconducting behavior by annealing in Ar atmosphere. Moreover, hysteresis loop and voltage-jump were observed in the I-V characteristic of the annealed Al/Bi-2212 structure in Ar atmosphere. These results show that the direction of current

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flow is changed from in-plane to out-of-plane by the selective reduction of the Bi-2212 single crystal due to the oxidation of the Al and that IJJs can be fabricated without etching process. The latter method is more advantageous to integration of superconducting circuit due to the high controllability of selective reduction.

Keywords: $Bi_2Sr_2CaCu_2O_{8+\delta}$ single crystal; intrinsic Josephson junctions; hydrogen annealing; Gibbs free energy

1. Introduction

Josephson effect in high-temperature superconductors has attracted attention due to its potential applications to future technologies [1, 2]. However, short coherence length of the high-temperature superconductor hinders the fabrication of Josephson junctions [3-5]. There are the stacks of superconducting CuO_2 double layers (3 Å) and insulating BiO and SrO layers (12 Å), so-called intrinsic Josephson junctions (IJJs) in $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) single crystals [6, 7]. Focused ion beam (FIB) and Ar-ion etching, which can form precise patterns is one of the most popular fabrication method for IJJs [8, 9]. Ar-ion etching is a fabrication technique that enables to control one unit of IJJ [9]. However, the theoretically predicted performance of the IJJs was not attained due to difficulty in fabrication of the Bi-2212 crystal without introduction of damage during the etching process [10-13]. Moreover, throughput of FIB (and Ar-ion etching) process is slow and the introduction of FIB equipment costs high. Therefore, establishment of fabrication process of IJJs without FIB process is attractive.

In this paper, IJJs were fabricated without FIB process by introduction of an oxygen-depleted layer to the surface of the Bi-2212 single crystal. This could be achieved by annealing the Bi-2212 single crystal in reductive atmosphere of H_2 gas. In addition, the oxygen-depleted layer could be introduced with higher controllability by deposition of metals with low Gibbs free energy and raising the temperature to exceed the activation energy for oxygen ions to move from Bi-2212 to the metal.

2. Experimental

Bi-2212 single crystals were grown using the vertical Bridgman method and were cleaved in the ambient to produce thin plates with typical dimensions of $5.0\times1.0\times0.02$ mm^3 [14,15]. All the cleaved crystals were annealed in flowing O_2 at 500 °C for 20 min to induce uniform oxygen content. The Pt (or Au) electrodes (EL) for four-terminal measurement were deposited side by side on the surface of the Bi-2212 single crystal by sputtering method, where the pairs of outer and inner electrodes were used as the current and voltage terminals, respectively. The samples were annealed in Ar, Ar+H_2 (Ar: H_2 = 19:1) or O_2 atmosphere to control oxygen content. Moreover, the Au or Al was deposited between the voltage terminals. The sample on which Au or Al was deposited between the voltage terminals is referred to as Au/Bi-2212 or Al/Bi-2212 structures. The samples were annealed in Ar atmosphere at between 200 and 500 °C to exceed the activation energy for oxygen ions to move from Bi-2212 to the electrode with low Gibbs free energy. The effects of annealing on resistivity-temperature (ρ-T) and current-voltage (I-V) characteristics were measured.

3. Results and Discussion

Figure 1(a) shows ρ-T characteristics of the Bi-2212 single crystal with electrodes for four-terminal measurement, where the as-prepared sample (circles) and those annealed in Ar atmosphere at 200 (triangles), 300 (squares), 400 (open circles) and 500°C (open triangles) for 60 min were shown.

Schematic of device structure is shown in the inset. All the ρ-T characteristics showed metallic (d/dT > 0) behavior and almost no change in resistivity and critical temperature (Tc) compared with the change caused by Ar+H_2 annealing (Fig. 1(b)). Figures 1(b) and 1(c) show ρ-T and I-V characteristics of as-prepared (circles) and those annealed in Ar+H_2 (triangles) and in O_2 (squares) atmosphere at 500 °C for 10 min, respectively. Here, the as-prepared sample was annealed in Ar+H_2 atmosphere after a series of measurements, followed by the O_2 annealing. The metallic ρ-T characteristic changed to semiconducting (d/dT<0) by annealing the sample in Ar+H_2 atmosphere. In accordance with the change in the ρ-T characteristics, the voltage-jump was not observed in I-V characteristics of the as-prepared sample when current was ramped up from 0 to 0.40 A, whereas hysteresis loop and voltage-jump, which are peculiar to IJJs [16,17], were observed in the I-V characteristic of the sample annealed in Ar+H_2 atmosphere. Both ρ-T and I-V characteristics recovered to those of the as-prepared sample by annealing the sample in O_2 atmosphere. This result suggests that current direction was changed from in-plane (// ab) to out-of-plane (// c) by annealing the sample in Ar+H_2 atmosphere. It is known that Bi-2212 single crystals are reduced by Ar+H_2 annealing and the superconductivity of the reduced area is suppressed [18, 19]. Therefore, the surface of the Bi-2212 single crystal except for the masked area with the electrodes was reduced by Ar+H_2 annealing. As a result, the change in the direction of the current was caused due to the detour avoiding the reduced area as shown in the inset of Fig. 1(c). On the other hand, the reduced area formed in the Ar+H_2 annealed sample was re-oxidized and superconductivity of the area recovered by O_2 annealing.

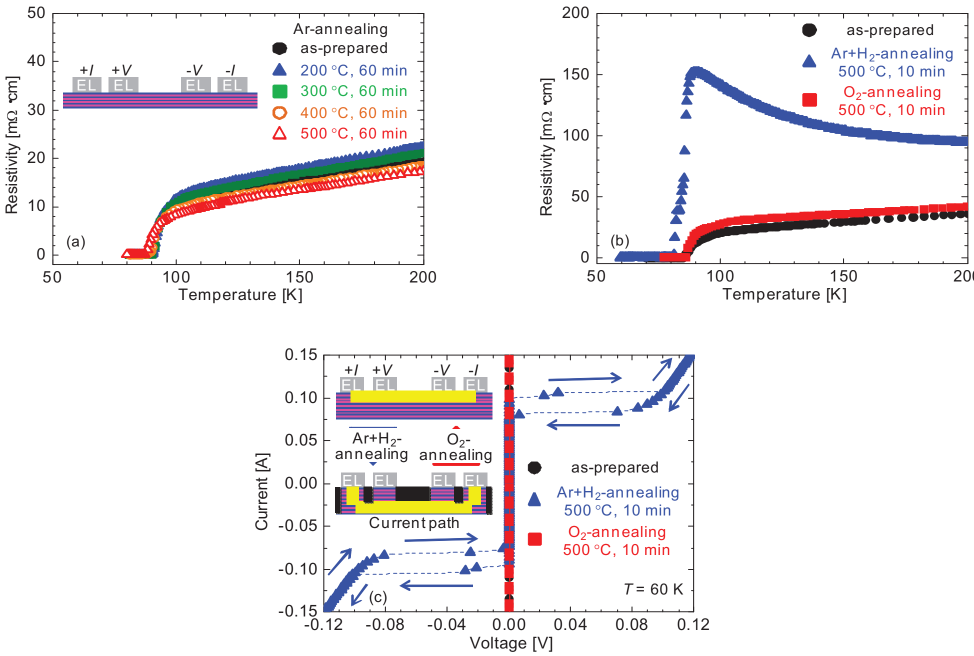


Fig. 1. (a) The dependence of ρ-T characteristics of Bi-2212 single crystal on the Ar annealing temperature. Schematic of device structure is shown in the inset. (b) ρ-T characteristics of the as-prepared sample and those annealed in Ar+H_2 and O_2 atmospheres. (c) I-V characteristics of as-prepared sample and those annealed in Ar+H_2 and O_2 atmospheres. Schematic of current path within the Bi-2212 single crystal is shown in the inset. The shadowed area in Bi-2212 single crystal shows the area where superconductivity was suppressed due to Ar+H_2 annealing.

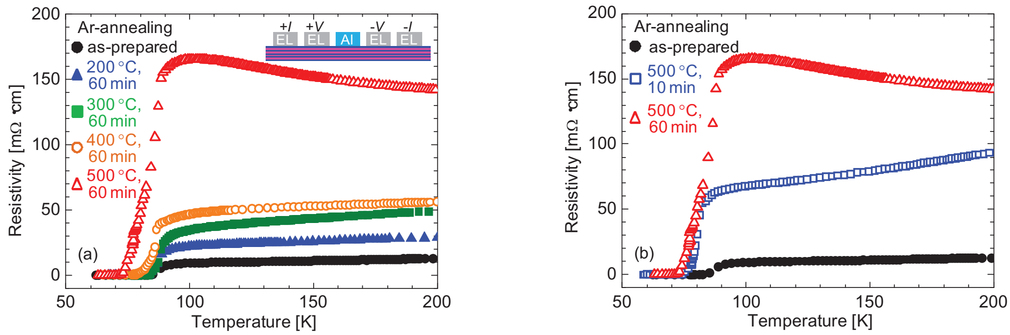


Fig. 2. ρ-T characteristics of the Al/Bi-2212 structure as a function of Ar annealing (a) temperature and (b) time. Schematic of device structure is shown in the inset.

As a result, the direction of current flow returned from out-of-plane to in-plane as shown in the inset of Fig. 1(c). That is why the ρ-T and I-V characteristics of the O_2 annealed sample almost agreed with those of the as-prepared sample.

The H_2 annealing is disadvantageous in integration of superconducting circuit consisting of IJJs, because H_2 gas reduces the whole surface of Bi-2212 single crystal except for the masked area. The method for selective reduction of a Bi-2212 single crystal is necessary.

Figure 2(a) shows the ρ-T characteristics of the as-prepared Al/Bi-2212 structure (circles) and those annealed in Ar atmosphere at 200 (triangles), 300 (squares), 400 (open circles) and 500 (open triangles) °C for 60 min. Schematic of the device structure was shown in the inset. The ρ-T characteristic for the as-prepared sample showed metallic behavior. The resistivity increased with increasing Ar-annealing temperature and the ρ-T characteristic changed from metallic to semiconducting behavior at the Ar-annealing temperature of 500 °C. However, T_c decreased from 84 (as-prepared sample) to 70 K by Ar-annealing at 500 °C for 60 min. It is effective to shorten annealing time in reducing the loss of T_c. Figure 2(b) shows ρ-T characteristics of the as-prepared Al/Bi-2212 structure (circles) and those after Ar annealing for 10 min (open squares) and 60 min (open triangles). Resistivity increased with increasing annealing time. On the other hand, T_c decreased with increasing annealing time and improved from 70 K to 74 K by decreasing annealing time from 60 min to 10 min.

Figure 3 shows the ρ-T characteristics of the as-prepared Au/Bi-2212 structure (circles) and that annealed in Ar atmosphere at 500 °C for 10 min (open triangles). The device structure is shown in the inset.

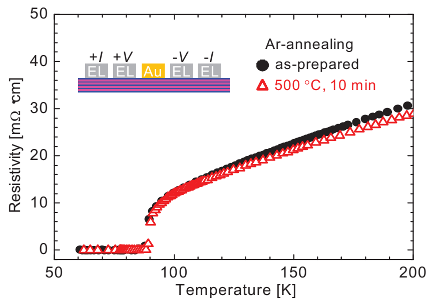
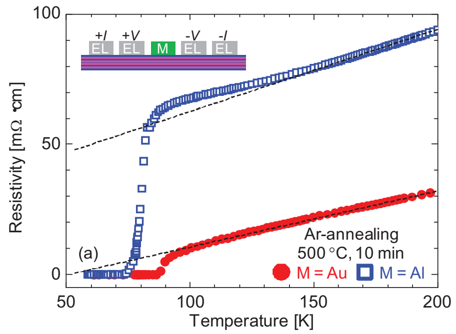


Fig. 3. ρ-T characteristics of the as-prepared Au/Bi-2212 structure (circles) and that annealed in Ar atmosphere at 500 °C for 10 min. Schematic of device structure is shown in the inset.

The ρ-T characteristics of the as-prepared Au/Bi-2212 structure showed metallic behavior and almost agreed with that of the annealed in Ar atmosphere. No significant difference in T_c was observed. The Gibbs free energies of Au and Al at 300 K are -42.447 and -1681.675 kJ/mol [20], respectively, which shows Al is easy to be oxidized compared with Au. Therefore, the increase of the resistivity in the Al/Bi-2212 structure by Ar annealing is suggested to be caused by reduction of the Bi-2212 single crystal due to oxidation of the Al.

Figures 4(a) and (b) shows the ρ-T and I-V characteristics of the Al/Bi-2212 (squares) and Au/Bi-2212 (circles) structures after annealing in Ar atmosphere at 500 °C for 10 min, respectively. The ρ-T characteristic of the Au/Bi-2212 structure showed metallic behavior, whereas the ρ-T characteristic of the Al/Bi-2212 structure shows weak semiconducting behavior. Hysteresis loop and voltage-jump were observed in the I-V characteristic of the Al/Bi-2212 structure, whereas they were not observed in the Au/Bi-2212 structure. These results show that the direction of current flow is changed from in-plane to out-of-plane by the selective reduction of the Bi-2212 single crystal due to the oxidation of the Al and that IJJ can be fabricated without FIB process, as shown in the inset of Fig. 4(b). The reduction degree and the thickness of the oxygen-depleted layer can be controlled by changing annealing conditions or metals used as reductants. Considering these properties and employing photolithography technology, it is expected that not only IJJs but also a whole of superconducting integrated circuit containing IJJs can be fabricated.



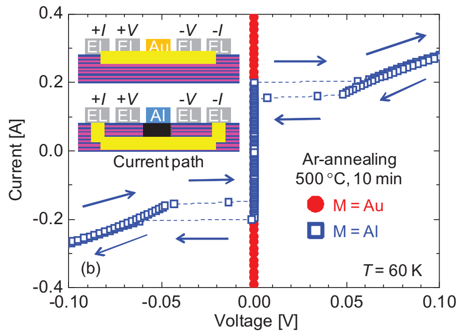


Fig. 4. (a) ρ-T and (b) I-V characteristics of the Al/Bi-2212 and Au/Bi-2212 structures after annealing in Ar atmosphere at 500 °C for 10 min. The shadowed area in Bi-2212 single crystal is the area where superconductivity was suppressed by reduction of the Bi-2212 due to oxidation of the Al.

4. Conclusions

IJJs were fabricated without etching process by introduction of an oxygen-depleted layer to the surface of the Bi-2212 single crystal. The oxygen-depleted layer can be formed by annealing the Bi-2212 in reductive gas atmosphere. In addition, by depositing a metal with low Gibbs free energy and raising the temperature to exceed the activation energy for oxygen ions to move from Bi-2212 to the metal, selective introduction of the oxygen-depleted layer to an arbitrary area becomes possible.

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